Electroanalysis with Controlled Cathode Potential of Metallic Copper Applied to Fabrics as Metallo-Organic Fungicides

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Abstract

A method is described for the electrolytic determination of copper in fabrics treated with organo-copper fungicides. The samples investigated contained fire retardants as metallic oxides, among which were those of antimony, calcium, zinc, and iron. Antimony offers the greatest interference in the electrolytic determination of copper. This interference was eliminated by depositing the copper from ammonium tartrate solution with careful control of the cathode potential, using a laboratory potentiometer to measure the voltage. Data are presented showing that copper may be electroplated from ammonium tartrate solutions, containing a six-fold greater concentration of antimony, with a cathode potential of — 0.60 volts. Standard deviations for analysis of these solutions were small ($\pm$ 0.001 mg. Cu/ml.), giving an error term of 0.05% (standard dev. of the mean, σ/mean determination $\times$ 100). Results are also given for analyses of fabrics containing copper-8-quinolinolate and copper naphthenate singly or in mixture. Standard deviations computed for these analyses also were small. A rapid and safe method for digesting cloth samples with sulfuric and perchloric acids is described.

Introduction

Application of fire retardants as metallic oxides to fabrics along with copper fungicides (ranging in concentration from 0.09 to 0.5% copper by weight of the fabric) creates a problem of analysis of the copper metal in the presence of other metals. The electrolytic determination of copper in the usual manner from solutions containing dilute sulfuric acid as electrolyte is unsuitable when antimony is present. The normal potentials of copper and antimony are close enough to require more careful control of the electrolysis. The following values of these potentials are given by Latimer [5]:

$$Cu^{++} + 2e = Cu \quad E^0 = +0.337v \quad (1)$$

$$SbO^+ + 2H^+ + 3e = Sb + H_2O$$
$$E^0 = +0.212v \quad (2)$$

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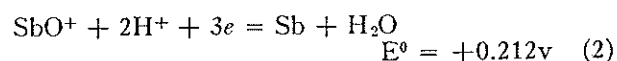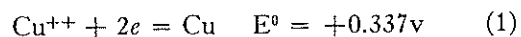
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Furman [2] separated copper and antimony by depositing copper from fluoride solution after oxidizing antimony to the pentavalent state with potassium persulfate. Presumably the effect of fluoride was to make the reduction potential of antimony more negative by forming a stable complex, thus preventing deposition of antimony. Electrolyses with these fluoride solutions necessitated the use of paraffin lined beakers and cover glasses.

For best results in the separation of copper and antimony, the use of a complexing agent can be supplemented by the technique of electrolysis with control of the cathode potential. This technique [1] consists of adjusting the applied potential of an electrolytic cell to maintain the potential of the cathode, with respect to some reference electrode, constant at some desired value. The cathode potential chosen lies at some value between the deposition potentials of the two metals to be separated. Thus Schoch and Brown [8] successfully separated copper and antimony by using an electrolyte containing hydrochloric acid and tartaric acid, and by maintaining a cathode potential of −0.50 to −0.65 volts. A somewhat more accurate procedure was worked out by Lingane [6]. It consists of using an electrolyte containing sodium tartrate and tartaric acid, and a cathode potential of −0.36 volts vs. the saturated calomel electrode.

The method which will be described for the determination of copper in fabrics treated with a fungicide is essentially that given by Lingane for metallic samples. The composition of electrolyte and conditions of electrolysis were changed slightly because of the nature of the sample studied. The cloth samples were digested with a mixture of perchloric and sulfuric acids. The insoluble calcium sulfate formed was removed by filtration. The excess acid was neutralized with ammonia and a slight excess of ammonia was added. Antimony was thus partially precipitated as the hydroxide and was removed by the filtration procedure. After adding the ammonium tartrate to the filtrate and adjusting the pH of the solution with sulfuric acid, the electrolysis was carried out at a controlled cathode potential.

A high pH favors the electrolytic separation of copper and antimony. This is shown in Equations 1 and 2. Hydrogen ion affects the potential of antimony, changing it to more negative values. Lingane chose a pH of 4.0–4.5 as the optimum value for the separation of copper from tin and antimony. Experimental investigation in this laboratory established that a pH of 5–6 was suitable for the electro-

lyte being discussed in the present work. At this pH, and with a concentration of 12 g. ammonium tartrate/200 ml. electrolyte, polarigraphic studies in this laboratory showed that copper is deposited at a cathode potential of −0.60 volts vs. the saturated calomel electrode without interference by antimony.

Methods

Polarigraphy of Solutions Containing Copper and Antimony

A series of polarigrams was taken for copper and antimony in electrolytes containing sulfate and various concentrations of ammonium tartrate. It was necessary to establish the deposition potentials of copper and antimony in these solutions and to determine the effect of tartrate concentrations on the deposition potentials of these metals.

The polarigrams were carried out using a Sargent XXI pen recording polarigraph with dropping mercury electrode. All solutions contained 1% gelatin and were deoxygenated with nitrogen for 15 min. before each run. The concentration of copper as copper sulfate was always 6×10^{-4} M and that of antimony as antimony potassium tartrate 2×10^{-3} M. One of the supporting electrolytes used was 10% ammonium tartrate. The remaining three electrolytes contained 30% ammonium sulfate plus 3, 6, and 9% ammonium tartrate respectively. The 30% ammonium sulfate concentration was selected because preliminary studies on digesting cloth samples with perchloric-sulfuric acid mixtures showed that this amount of sulfate was left after digestion. The pH of each solution was adjusted to between 5 and 6 with ammonium hydroxide using pHydrion paper.

Polarigrams were run for copper and copper-antimony mixtures in the four above-mentioned solutions. In all cases a reduction wave was obtained for copper having a half-wave potential of approximately −0.40 volts vs. the saturated calomel electrode. When antimony was present its reduction wave began at −0.90 volts.

These results show that the presence of ammonium sulfate has little or no effect on the reduction potentials of copper or antimony in tartrate medium. Also, the concentration of ammonium tartrate can be varied a great deal without significant change in reduction potentials. From the results obtained, a supporting electrolyte was used, containing 30% ammonium sulfate and 6% ammonium tartrate, to determine whether copper would separate from antimony

by electroplating the copper at a controlled potential of about −0.60 volts vs. the saturated calomel electrode.

Electrolysis of Solutions Containing Copper and Antimony

In order to test the controlled potential electrolytic procedure, several runs were made on model solutions containing copper and antimony (Table I). Electrolyses were carried out using an Eberbach electrolyzer equipped with a rotating gauze anode and perforated cylindrical cathode of platinum. Control of the cathode potential was performed manually by means of a circuit composed of the cathode, a calomel electrode immersed in the electrolyte, and a Beckmann Model G pH meter set to give voltage readings (Figure 1).

Stock solutions of copper sulfate and of antimony potassium tartrate were prepared. Each of these solutions contained approximately 2 mg. of the respective metal/ml. Aliquots were added to a supporting electrolyte containing either 10% ammonium tartrate or 30% ammonium sulfate and 6% ammonium tartrate, the pH being adjusted to about 5–6 in each case. The results obtained are shown in Table I.

As seen in Table I, the precision of this method, as computed in terms of standard deviation, is good. All the copper plates obtained were pink in color without any visual evidence of antimony. The remaining electrolytes were tested qualitatively with potassium ferrocyanide to determine completeness of the electroplating of the copper. Potassium ferrocyanide was experimentally established to give a positive test for copper at a concentration of 4×10^{-2} but not at 2×10^{-2} mg./ml.

The copper content of the stock solution was also determined by titration using the iodine-thiosulfate procedure [4]. Sodium thiosulfate solution was standardized with both potassium dichromate and potassium iodate, giving a value of $0.1028\ N$ and $0.1029\ N$, respectively. This standard thiosulfate solution was then used to titrate the iodine liberated by oxidizing iodide with aliquots of the stock solution of copper. Four such titrations gave identical values of 2.011 mg. copper/ml. These are lower than the average value of 2.032 mg. obtained with the electrolytic procedure. No reason can be given

TABLE I.   Results for Determination of Copper in Solutions Containing Antimony, Using Tartrate and Sulfate as Supporting Electrolytes

Run no.	Supporting electrolyte	Ml. stock Cu* sol'n added	Ml. stock Sb† sol'n added	Found, mg. Cu	Found, mg. Cu/ml.
1	10% ammonium tartrate	5	30	10.16	2.032
2	10% ammonium tartrate	10	—	20.34	2.034
3	30% ammonium sulfate, 6% ammonium tartrate	5	10	10.18	2.036
4	30% ammonium sulfate, 6% ammonium tartrate	5	30	10.16	2.032
5	30% ammonium sulfate, 6% ammonium tartrate	10	50	20.32	2.032
6	30% ammonium sulfate, 6% ammonium tartrate	20	—	40.54	2.027

Average mg. Cu/ml.   2.032
Standard deviation of the mean (mg./ml.)   ±.001

* 2 mg. Cu as copper sulfate/ml.
† 2 mg. Sb as antimony potassium tartrate/ml.

at this time for this apparent discrepancy. However, the electrolytic results were considered to be sufficiently reliable to test the method using cloth samples.

Analysis of Fabric Treated With Copper-8-Quinolinolate

The fabrics taken for study were 12.29-oz. cotton duck treated with copper-8-quinolinolate, copper naphthenate, a mixture of these two fungicides, water repellents, and fire retardants. A large enough sample (5 g.) was used to assure reasonable accuracy when the copper content was low. Copper deposited on the cathode was weighed on a semimicro balance.

Several methods were tried for acid-digesting fabric samples. These included various ways of heating with mixtures of sulfuric and perchloric acids, in some cases with the aid of nitric acid. Ashing of samples was found to be inadequate because fusions occurred which significantly affected the copper determinations. The best method found was that described by Kahane [3] for the digestion of animal tissues. The adaptation by this laboratory of Kahane's method involved heating of the sample with sulfuric acid until the most easily oxidized materials in the fabric have been destroyed. Perchloric acid was then added dropwise, with continued heating, at such a rate that it was consumed as fast as it was added. This digestion is rapid and safe.

The digest was a colorless or slightly yellow liquid containing a white or gray residue. Upon dilution, treatment with ammonium hydroxide, and filtering, calcium sulfate was removed along with any iron (as hydroxide) and part of the antimony (as hydroxide). The filtrate containing the copper was then treated with ammonium tartrate, the pH adjusted, and electrolyzed.

An Eberbach electrolyzer was used for plating out the copper. The cathode potential was measured by means of a circuit composed of the cathode connected to the glass electrode terminal of a Beckmann model G pH meter and a saturated calomel electrode dipped into the electrolyzing solution and connected to the saturated calomel electrode-terminal of the pH meter. The pH meter was set to read potential. The cathode potential was kept constant at −0.6 volts vs. the saturated calomel electrode by manually adjusting the voltage across the electrolytic cell. A schematic diagram of the apparatus is shown in Figure 1.
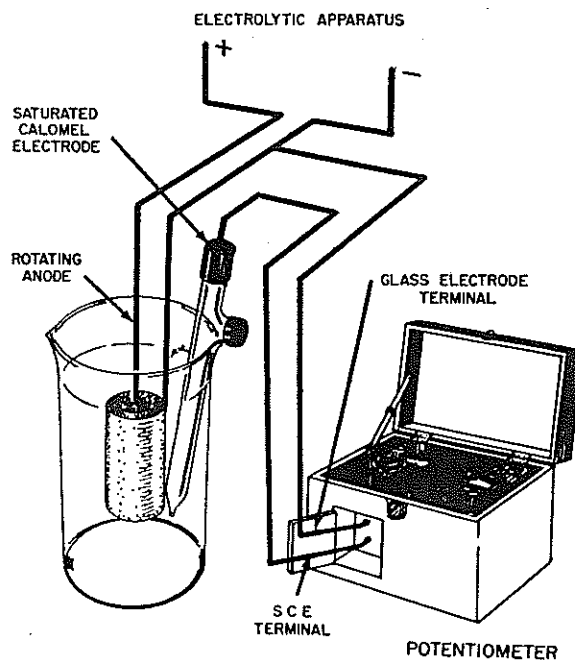

Fig. 1. Diagram of potentiometer-electroanalyzer circuit for the manual control of cathode potential.

Procedure

Weigh out a 5 g. sample, cut into ¼ in. squares, and place in a 300 ml. Erlenmeyer flask. Add 35 ml. concentrated sulfuric acid. Place a glass V, made from a 4 ml. glass rod, over the lip of the flask as support for a small short stemmed funnel, making sure that the stem touches the side of the flask. Heat the flask and contents to brisk reaction over a Meker burner in a hood provided with a safety shield. After about 45 min. start adding 72% perchloric acid dropwise, with continued heating, at such a rate (about 3 drops/min.) that the vigorous reaction continues. Oxidation should be complete in 30–40 min. after the addition of about 4 ml. perchloric acid. At this point remove the funnel and continue heating for an additional 30 min. to remove all traces of chlorine.

Cool and dilute (carefully!)[2] with 50 ml. of water. Make the solution slightly alkaline to litmus by dropwise addition of ammonia. Filter through No. 40 Whatman filter paper. Dilute the filtrate to approximately 200 ml. Add 12 g. ammonium tartrate and adjust the pH to between 5 and 6 with sulfuric acid.

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[2] Perchloric acid is a powerful oxidizing agent. Addition of water to a hot organic digest containing concentrated perchloric acid could result in an explosion. Cooling of the digest is imperative to minimize this hazard.

TABLE II. Determination of Copper in 12.29-Ounce Cotton Duck Treated with Copper Naphthenate and Copper-8-Quinolinolate, in Combination with Water Repellents and Fire Retardants

Run no.	Sample weight, g.	Cu applied to fabric as	% Cu found
1	5.163	none	.007
2	5.176	none	.001
Average % copper			.004
Standard deviation of mean			.003
3	5.038	Naphthenate	.346
4	5.075	Naphthenate	.335
5	5.024	Naphthenate	.354
6	5.045	Naphthenate	.352
7	5.037	Naphthenate	.347
Average % copper			.347
Standard deviation of mean			.003
8	5.247	8-Quinolinolate	.059
9	5.047	8-Quinolinolate	.060
10	5.095	8-Quinolinolate	.080
11	5.025	8-Quinolinolate	.065
Average % copper			.066
Standard deviation of mean			.005
12	5.425	Naphthenate and 8-Quinolinolate	.373
13	5.249	Naphthenate and 8-Quinolinolate	.388
14	5.215	Naphthenate and 8-Quinolinolate	.374
15	5.183	Naphthenate and 8-Quinolinolate	.376
Average % copper			.378
Standard deviation of mean			.003

Carry out the electrolysis using the arrangement shown in Figure 1. Slowly increase the applied potential until the cathode potential reaches −0.6 volts vs. the saturated calomel electrode. During the electrolysis the cathode potential will tend to change; frequent manual adjustments of the applied potential will be required. After an hour, test the electrolyte for copper by removing 2 ml. of solution and treating with 5% potassium ferrocyanide solution. If a pink color is obtained, continue the electrolysis. When no test is obtained for copper in the electrolyte, remove the cathode, rinse successively with distilled water and 95% ethyl alcohol. Dry the cathode at 105° C. for a few minutes. Cool and weigh.

Results

Table II gives results obtained with fabrics containing copper as the naphthenate and 8-quinolinolate. All of the deposits were bright pink in color. The results are reproducible with relatively small standard deviations. Since the actual copper content of the fabrics was not known, no analysis of the quan-

titative data can be given for the accuracy of these determinations. However, from the precision obtained in these runs and the fact that all the copper is known to have been deposited, this method affords reproducible determinations.

Using the manual control procedure as presented for adjusting the potential, there is some chance that the cathode potential may rise above −0.6 volts, causing antimony to deposit as a black plate. Whenever this occurred the electrolytic circuit was merely broken for about 10 min. The antimony then redissolved and the electrolysis was continued. The use of an automatic potentiostat [6] would eliminate this difficulty.

The time of electrolysis is usually about 3 hr. However, as many as four electrolyses have been run simultaneously by connecting the saturated calomel electrodes to the common terminal of the pH meter and switching in the desired cathode, whose potential is to be read. In this way the time required per run in doing several analyses can be shortened greatly.

Summary

The method of electroanalysis by control of the cathode potential has been applied successfully to the determination of copper in fabrics. No interference has been encountered with antimony or iron. Control of the cathode potential was carried out manually with the use of a Beckmann model G pH meter connected with a commercial electrolyzer.

Preparation of a sample of fabric for electroanalysis was easily and safely done using sulfuric and perchloric acids as oxidizing agents. This was accomplished by oxidizing a large part of the sample with sulfuric acid alone, then completing the digestion by dropwise addition of perchloric acid to the hot solution.

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